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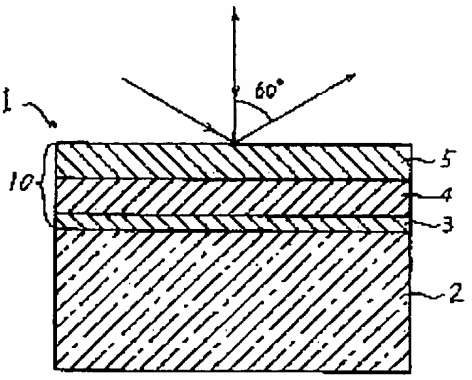
(54) LOW REFLECTION GLASS SHEET AND LOW REFLECTION LAMINATED GLASS SHEET FOR AUTOMOBILE USING THAT GLASS SHEET

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a low reflection glass sheet which has an antireflection function for oblique incident light and which can decrease reflection not only on the surface but on the rear surface.
SOLUTION: This low reflection glass sheet has a low reflection film 10 formed by successively laminating a light-absorbing film 3, high refractive index film 4, and low refractive index film 5 on one principal plane of a glass sheet. The light-absorbing film consists of a metal compd. The refractive index nH and the geometric film thickness dH of the high refractive index film range 2.0 to 2.5 and 60 to 150 nm, respectively. The refractive index nL and the geometric film thickness dL of the low refractive index film are 1.44 to 1.48 and 85 to 110 nm, respectively. Thus, the obtd. glass sheet shows decrease in the reflectance for visible rays for incident light in the perpendicular direction and oblique direction of the sheet.



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CLAIMS

[Claim(s)]
[Claim 1] In the low reflective glass plate which has the low reflective film which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on one principal plane of a glass plate Said light absorption film consists of metallic compounds. Said high refractive-index film the refractive index nH and geometric thickness dH They are nH=2.0-2.5 and dH=60-150nm. Said low refractive index film the refractive index nL and geometric thickness dL It is referred to as nL=1.44-1.48 and dL=85-110nm, and the light reflection factor to the vertical-incidence light from said low reflective film surface side is 5% or less. The low reflective glass plate characterized by for the light reflection factor to 60-degree incident light by the side of said low reflective film surface (include angle when making a perpendicular into 0 degree) being 12% or less, and the light reflection factor to the vertical-incidence light from said glass plate side being 10% or less.
[Claim 2] When N1=n1-i-k [the complex index of refraction of said light absorption film]1 (n1 expresses the real part of a refractive index with the imaginary part of a refractive index, and k1 expresses an extinction coefficient) is written in a low reflective glass plate according to claim 1, n1 and k1 in the wavelength of 550nm -- 1.6 <=n1 <=3.5, 0.3 <=k1 <=2.0, and the thickness d1 with said light absorption film geometric [that come out and it is] -- 1<=20nm of 3 nm<=d -- coming out -- a certain low reflective glass plate.
[Claim 3] It is the low reflective glass plate with which said light absorption film uses the ingredient of the either the nitride of NiSiON (acid nitride of nickel silicide), SiC (silicon carbide), SiCON (acid nitride of silicon carbide), and Ti, Zr, Hf, Ta and Nb or the acid nitrides as a principal component in a low reflective glass plate according to claim 1 or 2.
[Claim 4] claims 1-3 -- the low reflective glass plate whose light permeability of said low reflective glass plate is 70% or more in a low reflective glass plate given in either.
[Claim 5] claims 1-3 -- the low reflective glass plate which prepared the film which has the oxygen cutoff engine performance further between said light absorption film and said high refractive-index film in the low reflective glass plate given in either.
[Claim 6] The low reflective glass plate which prepared the film which has the oxygen cutoff engine performance further between said glass plates and said light absorption film in a low reflective glass plate according to claim 5.
[Claim 7] The film which has said oxygen cutoff engine performance in a low reflective glass plate according to claim 5 or 6 is a low reflective glass plate whose value of said X it consists of silicon nitride as a principal component, or consists of acid silicon nitride expressed as SiNxO 1-x, and is 0.6<=X<1.0.
[Claim 8] claims 1-3 -- the low reflective glass plate which is the film which uses at least one or more sorts as a principal component for the ingredient with which said high refractive-index film was chosen from titanium oxide, tantalum oxide, niobium oxide, and tin oxide in a low reflective glass plate given in either.
[Claim 9] claims 1-3 -- the low reflective glass plate which is the film with which said low refractive index film uses oxidation silicon as a principal component in a low reflective glass plate given in either.

[Claim 10] claims 1-9 -- the low reflective glass laminate plate for cars which it is the low reflective glass laminate plate for cars which pasted up the field of another side of the low reflective glass plate of a publication, and the transparence glass plate other than said glass plate on either by the interlayer made of thermoplastics, and the light permeability of this glass laminate plate is 70% or more, and is characterized by making the forming face of the low reflective film into the interior-of-a-room side of a car.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the low reflective glass plate which is a low reflective glass plate with which acid resisting to oblique-incidence light was also taken into consideration, and is further applied also to bending or strengthening processing about a low reflective glass plate.
[0002]
[Description of the Prior Art] In order to reduce the front face of an optic or CRT, and surface reflection of the filter for a display conventionally, the proposal of many antireflection films is made.
[0003] As the one solution means, there is an antireflection film using an optical thin film. this antireflection film -- being related -- many explanatories (for example, Sadaji Yoshida and Hiroyoshi Yajima collaboration: "a thin film and an optical device" --) (1994) University of Tokyo Press, H. A.Macleod:"Thin-Film Optical Filters and 2nd Editon", Adam Hilger Ltd, Bristol, T.J.Coutts Edited:"ACTIVE AND PASSIVE THIN FILM DEVICES", p334-p344, (1978), ACADEMIC PRESS, H.KPULKER:"Coatings on Glass", p399-p407, (1984), Explanation is made with ELSEVIER and a handbook (for example, a "thin film handbook", p818 - Ohm-Sha).
[0004] Furthermore, the case where a metal membrane is included as absorption film in optical multilayers is also explained by "the thin film and the optical device", and the "thin film handbook" which were mentioned above.
[0005] By the way, the light absorption nature acid-resisting object which consists of two-layer film of the light absorption film and the silica film on a base is indicated by JP,9-156964,A as an acid-resisting technique in CRT etc. In detail, the geometric thickness of the light absorption film is 5-25nm, and the geometric thickness of the silica film may be 70-110nm. Furthermore, it is shown that the light absorption film is film which uses as a principal component the nitride of at least one sort of metals chosen from the group which consists of titanium, a zirconium, and a hafnium.
[0006] Furthermore, the light absorption nature acid-resisting object which consists of the light absorption film, high refractive-index film, and three layer membranes of the silica film on a base is indicated as the 2nd invention. In detail, the geometric thickness of the light absorption film is [the geometric thickness of 15-25nm and the high refractive-index film] 10-40nm, and the geometric thickness of the silica film may be 50-90nm.
[0007] Calling an oxidization barrier layer between the further above-mentioned light absorption film and the silica film to above-mentioned JP,9-156964,A, and preparing the layer which uses as a principal component the metal or metal nitride whose geometric thickness is 1-20nm is shown. The film which uses as a principal component at least one sort of metals chosen from the group which specifically consists of chromium, molybdenum, a tungsten, vanadium, niobium, a tantalum, zinc, nickel, palladium, platinum, aluminum, an indium, tin and the film that uses as a principal component at least one sort of metals chosen from the group which consists of silicon, the film which uses these nitrides as a principal component or titanium, a zirconium, and a hafnium be shown. It is supposed that the film which uses the nitride of silicon or silicon as a principal

component especially is desirable.
[0008] Similarly, the same technique as JP,9-156964,A is indicated by JP,10-96801,A and JP,10-230558,A as an acid-resisting technique in CRT etc.
[0009]
[Problem(s) to be Solved by the Invention] On the other hand, the low reflex function is called for also in the windowpane used for cars, such as an automobile. Especially as for the window shield glass of an automobile, the configuration top dashboard will be reflected. This reflect lump serves as a noise at the time of recognizing the information from the external world through a windowpane for a driver. When a solar radiation beam of light is strong, this reflect lump becomes remarkable still more.
[0010] Moreover, window shield glass inclines further and is increasingly attached by the request on a design and aerodynamics. Therefore, the effect of a reflect lump of a dashboard has been increasing the degree increasingly.
[0011] Especially in Nighttime, a reflect lump of the light from the instruments of a dashboard, the car navigation equipment formed around a dashboard becomes very offensive to the eye for a driver.
[0012] Furthermore, the visibility is made to fall when there is a reflect lump also by automobile equipped with HUD equipment (HUD) in addition to the information which should be displayed.
[0013] In transparence bases, such as a windowpane used for cars, such as an automobile, in order to give a low reflex function, when forming the antireflection film by the optical thin film, the following troubles come out.
[0014] That is, the antireflection film stated with the explanatory mentioned above is mainly discussed in acid resisting about a transparent-body front face and vertical-incidence light. About the synthetic antireflection film taken into consideration, no explanation is given also about the function to prevent the reflection from acid resisting to oblique-incidence light, and a rear face in case the transparent body is tabular.
[0015] First, with the window shield glass of an automobile, the acid-resisting function to oblique-incidence light becomes important on the configuration especially. p821 of an above-mentioned "thin film handbook" "the incident angle dependency of a reflection factor must also be taken into consideration in selection of an antireflection film. Since a reflection factor begins to increase by whenever [such small incident angle / that it generally becomes multilayers], cautions are required when using a multilayer antireflection film. Indication with " is made. However, no concrete solution approaches etc. are shown.
[0016] Below, the antireflection film which can reduce the reflection from a transparent-body rear face will be considered. In the glass plate of ns=1.52, about 4% of reflection arises in the front face and rear face, respectively. It is the antireflection film mentioned above about the reflection in a front face, and reflection can be prevented. However, when reducing the reflected light from a rear face is considered, it is impossible to attain it only with the antireflection film mentioned above in the place which changed the design of a metaphor optical thin film. It is because the antireflection film mentioned above is an optical thin film which consists of a dielectric which is the transparent body fundamentally.
[0017] Then, the case where the absorption film is included in optical multilayers is examined. If light permeability is not asked at this time, a metal membrane can be used as absorption film. However, for the application of the window shield glass of an automobile etc., having a certain light permeability more than fixed may be called for.
[0018] In such a case, since absorbing power of a metal membrane is too large and light permeability becomes small too much, it cannot use as absorption film. If it is going to be satisfied with a metal membrane of light permeability, it is unknown in the ability to form as continuation film by becoming very thin thickness. Moreover, by such film, there is a problem also from a viewpoint of endurance, such as corrosion resistance. For the application of an automobile or construction, especially the problem of endurance is important.
[0019] It is shown by above-mentioned JP,9-156964,A that it is the film which uses as a principal component the nitride of at least one sort of metals chosen from the group which consists of titanium, a zirconium, and a hafnium as light absorption film.

[0020] Furthermore, the film with which above-mentioned JP,10-96801,A also contains gold as light absorption film, A gold film, the alloy film which contains gold 50% of the weight or more, the nitride film of this alloy, the acid nitride film of this alloy, The carbide film of this alloy or the carbon nitride film of this alloy, the film containing copper, a copper film, The copper nitride film, the copper acid nitride film, the copper carbide film, the copper carbon nitride film, the alloy film that contains copper 50% of the weight or more, the nitride film of this alloy, the acid nitride film of this alloy, the carbide film of this alloy, or the carbon nitride film of this alloy is shown.
[0021] However, the technique indicated by JP,9-156964,A and JP,10-96801,A which were mentioned above, and JP,10-230558,A is mainly an acid-resisting technique in CRT etc., is considered to aim at acid resisting of the incident light from a perpendicular direction, and is touched with nothing about acid resisting about oblique-incidence light.
[0022] Moreover, bending and doubling processing are performed and the windowpane for automobiles is usually applied. When forming an antireflection film in a glass plate first and performing these processings after that, an antireflection film will pass through a heating process. Therefore, an antireflection film will be asked for thermal resistance.
[0023] In order to solve a technical problem which was described above, it is in offering the low reflective glass plate which may have not only vertical-incidence light but an acid-resisting function to oblique-incidence light by combining the light absorption film which absorbs and reduces the reflection from a rear face as a purpose of this invention in the glass plate which is the tabular transparent body, and the optical multilayers which consist of high refractive-index film and a low refractive index film.
[0024] Moreover, it is in offering the low reflective glass plate which has the antireflection film taken into consideration also about thermal resistance.
[0025] It is also offering the low reflective glass plate for automobiles using a these low reflective glass plate furthermore.
[0026]
[Means for Solving the Problem] Namely, this invention is set to the low reflective glass plate which has the low reflective film which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on one principal plane of a glass plate as claim 1. Said light absorption film consists of metallic compounds. Said high refractive-index film the refractive index nH and geometric thickness dH They are nH=2.0-2.5 and dH=60-150nm. Said low refractive index film the refractive index nL and geometric thickness dL It is referred to as nL=1.44-1.48 and dL=85-110nm, and the light reflection factor to the vertical-incidence light from said low reflective film surface side is 5% or less. It is the low reflective glass plate characterized by for the light reflection factor to 60-degree incident light (include angle when making a perpendicular into 0 degree) from said low reflective film surface side being 12% or less, and the light reflection factor to the vertical-incidence light from said glass plate side being 10% or less.
[0027] Moreover, when it writes as claim 2 N1=n1-i-k [the complex index of refraction of said light absorption film] I (n1 expresses the real part of a refractive index with the imaginary part of a refractive index, and k1 expresses an extinction coefficient) in a low reflective glass plate according to claim 1, it comes out, and it is, and 1.6 <=n1 <=3.5, 0.3 <=k1 <=2.0, and the geometric thickness d1 of said light absorption film come out 1<=20nm of 3 nm<=d, and n1 and k1 in the wavelength of 550nm are a certain low reflective glass plate.
[0028] Furthermore, said light absorption film is a low reflective glass plate which uses the ingredient of the either the nitride of NiSiON (acid nitride of nickel silicide), SiC (silicon carbide), SiCON (acid nitride of silicon carbide), and Ti, Zr, Ta and Nb or the acid nitrides as a principal component as claim 3 in a low reflective glass plate according to claim 1 or 2.
[0029] moreover -- as claim 4 -- claims 1-3 -- in a low reflective glass plate given in either, it is the low reflective glass plate whose light permeability of said low reflective glass plate is 70% or more.
[0030] further -- as claim 5 -- claims 1-3 -- in a low reflective glass plate given in either, it is the low reflective glass plate which prepared the film which has the oxygen cutoff engine performance further between said light absorption film and said high refractive-index film.

[0031] Moreover, it is the low reflective glass plate which prepared the film which has the oxygen cutoff engine performance further between said glass plates and said light absorption film in a low reflective glass plate according to claim 5 as claim 6.
[0032] Furthermore, as claim 7, the film which has said oxygen cutoff engine performance in a low reflective glass plate according to claim 5 or 6 consists of silicon nitride as a principal component, or consists of acid silicon nitride expressed as SiNxO 1-x, and it is the low reflective glass plate whose value of said X is 0.6<=X<1.0.
[0033] moreover -- as claim 8 -- claims 1-3 -- in a low reflective glass plate given in either, said high refractive-index film is a low reflective glass plate which is the film which uses at least one or more sorts as a principal component for the ingredient chosen from titanium oxide, tantalum oxide, niobium oxide, and tin oxide.
[0034] further -- as claim 9 -- claims 1-3 -- in a low reflective glass plate given in either, said low refractive index film is a low reflective glass plate which is the film which uses oxidation silicon as a principal component.
[0035] moreover -- as the glass laminate plate using the above low reflective glass plate -- claims 1-9 -- with the field of another side of the low reflective glass plate of a publication to either It is the low reflective glass laminate plate for cars on which the transparence glass plate other than said glass plate was pasted up by the interlayer made of thermoplastics, and the light permeability of this glass laminate plate is 70% or more, and it is the low reflective glass laminate plate for cars characterized by making the forming face of the low reflective film into the interior-of-a-room side of a car.
[0036] Since it has moderate light permeability as light absorption film first and endurance is searched for, not a metal but metallic compounds are suitable. As a concrete ingredient, a nitride or an acid nitride of NiSiON (acid nitride of nickel silicide), SiC (silicon carbide), SiCON (acid nitride of silicon carbide), and Ti, Zr, Hf, Ta and Nb etc. can be illustrated.
[0037] The thin film which consists of the nitride or acid nitrides of transition metals which were mentioned above, such as Ti, Zr, Hf, Ta, and Nb, is an ingredient included in the range of the optical constant which there is no strong absorption like a metal membrane, and was indicated to claim 2. Moreover, since they have the outstanding endurance and thermal resistance, they are desirable ingredients.
[0038] The high refractive-index film should just be an ingredient which has the refractive index of nH=2.0-2.5 next. as the ingredient which specifically has the refractive index of n=2.0-2.5 -- In 2O3 (2.0), Nd2O3 (2.1), and ZrO2 (2.1), CeO2 (2.2), TiO2 (2.2-2.7), ZnS (2.35) and Ta2 -- O5 (2.1) and Nb2 -- O5 (2.2), SnO2 (2.0), etc. are mentioned. Especially TiO2, Ta 2O5, Nb2O5, and SnO2 are preferably used the outstanding endurance or in respect of thermal resistance.
[0039] Furthermore, a low refractive index film should just be an ingredient which has the refractive index of nL<1.5. The ingredient which furthermore has the refractive index of nL=1.44-1.48 is desirable. As an ingredient of n< 1.5, MgF2 (1.38), SiO2 (1.46), etc. mention, and, specifically, SiO2 has desirable **** in the viewpoint of endurance or abrasion-proof nature.
[0040] Moreover, the film which has the oxygen cutoff engine performance has the desirable film which uses as a principal component the silicon nitride or acid silicon nitride expressed as SiNxO 1-x.
[0041] In addition, in JP,9-156964,A and JP,10-96801,A which were mentioned above, an oxidization barrier layer is called between the light absorption film and the silica film, and the layer of Si whose geometric thickness is 1-20nm, or SiNx is prepared in it. In the explanation about this barrier layer, this barrier layer is supposed that it does not have semantics optically. therefore, the geometric thickness is set to 1-20nm, and should be made especially about 5nm or less -- ** -- it is carrying out.
[0042] However, by the oxygen cutoff film in this invention, even if the geometric thickness is 6nm or more and is 50nm or more, it does not interfere, so that more clearly than the below-mentioned example.
[0043]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.
(The 1st operation gestalt) The 1st operation gestalt of this invention is a low reflective glass

plate which consists of low reflective film which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on the glass plate substantially first.
[0044] (Example 1) The 1st operation gestalt is explained with reference to drawing 1 . The soda lime glass substrate of the usual presentation manufactured by the float glass process was first prepared as a glass substrate 2. Washing desiccation of this glass substrate was carried out by the usual technique, and the following examples and examples of a comparison were presented.
[0045] First, the light absorption layer 3 is formed. Said glass substrate 2 is set through an electrode holder in the inline-type magnetron sputtering system which has two or more chambers. Next, a rotary pump, and cryopump or a turbine pump is used, and the inside of a chamber is exhausted to 10-6Torr. It continued, the mixed gas of O2 and N2 was introduced in the chamber using the NiSi alloy target, and the NiSiON film was formed by reactive sputtering with the gas pressure of 3mmTorr(s).
[0046] Next, the high refractive-index film 4 is formed. O2 gas was introduced for said substrate with which the light absorption layer was formed in the chamber by another chamber of said sputtering system using Ti metal target, and TiO2 film was formed by reactive sputtering with the gas pressure of 3mmTorr(s).
[0047] Furthermore, a low refractive index film 5 is formed. O2 gas was introduced for said substrate with which the high refractive-index film was formed in the chamber by still more nearly another chamber of said sputtering system using Si metal target, and SiO2 film was formed by reactive sputtering with the gas pressure of 3mmTorr(s).
[0048] Thus, the low reflective glass plate 1 which has the low reflective film 10 which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on one principal plane of a glass plate was produced (refer to drawing 1). In addition, the thickness of each film is as having been shown in Table 1.
[0049] In addition, since each film mentioned above is produced by reactive sputtering, it contains the gas introduced into the film.
[0050] (Examples 2-6) An example 2 is the same film configuration as an example 1, and is an example to which the thickness of each film was changed. Or examples 3 and 4 introduce O2 gas in a chamber, using Ta metal target as high refractive-index film, are the gas pressure of 3mmTorr(s), and are examples which formed 2OTa5 film by reactive sputtering. Other film is the same as that of an example 1.
[0051] Furthermore, examples 5 and 6 introduce O2 gas in a chamber, using Sn metal target as high refractive-index film, are the gas pressure of 3mmTorr(s), and are examples which formed SnO2 film by reactive sputtering. Other film is the same as that of an example 1. The low reflective glass plate was produced as mentioned above. The thickness of each film in each example is as having been shown in Table 1. In addition, MFL of front Naka expresses the thing of a float glass plate which has green.
[0052] In addition, in examples 1-6, n1 and k1 of the NiSiON film which is light absorption film were 1.81 and 0.48, respectively. Moreover, although sputtering was performed in the gas ambient atmosphere required for a reaction in each film formation of the above-mentioned examples 1-6, it is also possible to mix Ar gas if needed. In this case, Ar gas will also be included in that film.
[0053]
[Table 1]

A fruit ******** Low refractive index film / quantity refractive-index film/(cutoff film) / light absorption film/(cutoff film) / example of a glass substrate (nm) (nm) (nm) (nm) (board thickness mm)
— 1 SiO2 /TiO2 / — /NiSiON/ — /MFL 95.9 / 96.6 / — / 14.3 / — / 4.22 SiO2 /TiO2/ — /NiSiON/ — /MFL 99.3 / 93.3 / — / 6.0/ — /4.23SiO2 / Ta2O5/ — /NiSiON/ — /MFL 94.2 / 93.0 / — / 12.4 / — / 4.24 SiO2 /Ta2O5/ — /NiSiON/ — /MFL 88.9 / 95.1 / — / 10.3 / — / 4.25 SiO2 /SnO2 / — /NiSiON/ — /MFL 96.2 / 97.2 / — / 12.1 / — / 4.26 SiO2 /SnO2 / — /NiSiON/ — /MFL 88.9 / 99.6 / — / 9.8 / — / 4.2

MFL:green float glass [0054] The optical property of the glass substrate produced as mentioned

above is shown in Table 2. In addition, the light permeability of a glass substrate MFL4.2 is 80.6%. Measurement of an optical property measures a transparency spectrum or a reflectance spectrum with a visible region spectrophotometer with an integrating sphere, and is JIS. R Based on the calculation approach of 3016, light permeability and a light reflection factor were computed. In addition, the reflection factor of 60-degree incident light by the side of a film surface (include angle when making a perpendicular into 0 degree) estimated the acid-resisting function to oblique-incidence light.
[0055]
[Table 2]

Fruit Permeability A film surface side reflection factor Glass side side ******** Tvis (%) Rfvis(%) 0 degree Rfvis(%) 60 degree The example of Rgvis(%) 0 degree
1 74.8 4.0 8.9 6.92 76.0 4.1 9.2 6.73 75.9 3.9 8.86.64 77.3 3.7 9.3 5.95 76.13.9 8.5 6.56 77.6 3.5 9.1 5.6

* Tvis(%):light permeability, the light reflection factor of the vertical-incidence light by the side of a Rfvis(%) 0-degree:film surface, the light reflection factor of 60-degree incident light by the side of a Rfvis(%) 60-degree:film surface, Rgvis(%) 0 degree : the light reflection factor of the vertical-incidence light by the side of a glass side. [0056] The low reflective glass plate of the examples 1-6 which are the 1st operation gestalten of this invention so that more clearly than Table 2 Light permeability of all is 74% or more, and the light reflection factor to the vertical-incidence light from a low reflective film surface side is 4% or less further. The light reflection factor to 60-degree incident light from said low reflective film surface side is 10% or less, and the light reflection factor to the vertical-incidence light from said glass plate side is 7% or less.
[0057] As mentioned above, the low reflective glass plate of the 1st operation gestalt of this invention is a low reflective glass plate with an acid-resisting function also not only to an acid-resisting function but the oblique-incidence light to vertical-incidence light, having the outstanding light permeability.
[0058] (The 2nd operation gestalt) The 2nd operation gestalt of this invention prepares the oxygen cutoff film between the light absorption film and the high refractive-index film in the low reflective glass plate which consists of low reflective film which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on the glass substrate first (refer to drawing 2).
[0059] (Examples 7-13) The 2nd operation gestalt is explained with reference to drawing 2 . The fundamental production approach applies to the 1st operation gestalt correspondingly. The glass plate (it expresses floor line) and above-mentioned MFL by the float engine performance of the usual soda lime presentation were used for the glass substrate 2. As light absorption film 3, the SiC film, SiCON film, and TiN film other than the NiSiON film were formed. Furthermore, the SiN film was formed as oxygen cutoff film 6.
[0060] Using the SiC ceramic target, the SiC film as light absorption film 3 introduced Ar gas in the chamber, is the gas pressure of 3mmTorr(s) and formed by performing sputtering. Similarly, using the SiC ceramic target, the SiCON film introduced the mixed gas of O2 and N2 in the chamber, is the gas pressure of 3mmTorr(s) and formed it by reactive sputtering. Moreover, using Ti metal target, the TiN film introduced N2 gas in the chamber, is the gas pressure of 3mmTorr(s) and formed it by reactive sputtering.
[0061] Next, Si metal target was used for the SiN film as oxygen cutoff film 6, and it introduced N2 gas in the chamber, is the gas pressure of 3mmTorr(s) and formed it by reactive sputtering. In addition, especially O2 has not introduced at the time of membrane formation of an SiN film. However, since it is very easy to combine Si with oxygen, if it forms membranes by the sputtering method, it will incorporate and keep the oxygen which remains in a chamber (reacting with oxygen), and will become the SiNO film. According to the sputtering method mentioned above, it checked by analysis that about 20% of oxygen was included in the film. Moreover, it can be said that it is therefore functioning as oxygen cutoff film in the strength of bonding strength with the oxygen of Si.
[0062] Next, like the 1st operation gestalt, the laminating of the high refractive-index film 4 and the low refractive index film 5 was carried out one by one, and the low reflective film 10 was

formed.
[0063] Furthermore, in order to investigate the thermal resistance of the obtained low reflective glass plate supposing heating in bending, strengthening processing, etc., the low reflective glass plate was calcinated for 10 minutes at 630 degrees C with the firing furnace. In addition, bending and strengthening processing of a soda lime glass plate are performed by heating at about 600 degrees C or more. The low reflective glass plate 20 was produced as mentioned above.
[0064] It seemed that in addition, n1 and k1 of the NiSiON film which is light absorption film, the SiC film, the SiCON film, and TiN **** were shown in Table 3 in examples 7-15. Moreover, the thickness of each film in each example is as having been shown in Table 4.
[0065]
[Table 3]

光学収納	n_1	k_1
NISION膜 :	1.81.	0.48
SIC膜 :	3.42.	0.46
SICON膜 :	2.93.	1.69
TIN膜 :	2.36.	1.52

[0066]
[Table 4]

A fruit ******** Low refractive index film / quantity refractive-index film/(cutoff film) / light absorption film/(cutoff film) / example of a glass substrate (nm) (nm) (nm) (nm) (nm) (board thickness mm)
— 7 SiO2 /TiO2 /SiN/NiSiON/ — / floor line 99.5/ 96.5 / 7.5 / 16.8 / —/3.08
SiO2 /TiO2 /SiN/SiC/ — / floor line 93.1 / 80.6 / 8.5 /6.3/ — / 3.09
SiO2/TiO2 /SiN/SiCON / — / floor line 92.2 / 68.3 / 13.4 / 15.2 / — / 3.010
SiO2 /TiO2 /SiN/TiN/ — / floor line 99.3 / 92.7 / 17.3 / 5.2 / — / 3.011
SiO2 /TiO2 /SiN/NiSiON/ — / MFL 99.1 / 94.6 / 8.0 / 12.8 / — / 4.212 SiO2 /Ta2O5 / SiN/NiSiON/ — / MFL 95.6 / 93.7 / 6.4 / 7.0 / — / 4.213 SiO2 /Ta2O5 / SiN/NiSiON/ — / MFL 105.5 / 94.6 / 30.5 / 10.3/ — / 4.2 — floor line: — float glass [0067] The optical property of the low reflective glass plate produced as mentioned above is shown in Table 5. In addition, the light permeability of glass substrate floor line3.0 is 89.8%.

[0068]
[Table 5]

Fruit Permeability A film surface side reflection factor Glass side side ******** Tvis (%) Rfvis(%) 0 degree Rfvis(%) 60 degree The example of Rgvis(%) 0 degree
7 76.0 4.0 9.2 8.48 80.7 4.0 9.5 8.39 84.0 4.2 10.4 6.910 72.0 4.0 9.1 9.011 75.3 4.2 9.0 6.612 75.8 4.1 8.9 6.813 76.7 4.0 8.9 6.0

[0069] The low reflective glass plate of the examples 7-13 which are the 2nd operation gestalten of this invention so that more clearly than Table 4 Light permeability of all is 72% or more, and the light reflection factor to the vertical-incidence light from a low reflective film surface side is 4% or less further. The light reflection factor to 60-degree incident light from said low reflective film surface side is 11% or less, and the light reflection factor to the vertical-incidence light from said glass plate side is 9% or less.
[0070] As mentioned above, the low reflective glass plate of the 2nd operation gestalt of this invention is a low reflective glass plate with an acid-resisting function also not only to an acid-resisting function but the oblique-incidence light to vertical-incidence light, having the outstanding light permeability. Furthermore, it is the low reflective glass plate which also has thermal resistance. Since the oxygen cutoff film 6 is formed between the light absorption film 3 and the high refractive-index film, when a low reflective glass plate is heated, in case the high

refractive-index film 4 and a low refractive index film 5 are formed, the oxygen from an ambient atmosphere can be intercepted.
[0071] (The 3rd operation gestalt) The 3rd operation gestalt of this invention forms the oxygen cutoff film 6 further between a glass substrate 2 and the light absorption film 3 in the above-mentioned 2nd operation gestalt first (refer to drawing 3).
[0072] (Examples 14-15) The 3rd operation gestalt is explained with reference to drawing 3 . The fundamental production approach applies to the 2nd operation gestalt correspondingly. The SiN film as oxygen cutoff film 6 prepared between a glass substrate 2 and the light absorption film 3 is the same as that of the approach stated with the 2nd operation gestalt. First, the laminating of the oxygen cutoff film 6, the light absorption film 3, the oxygen cutoff film 6, the high refractive-index film 4, and the low refractive index film 5 was carried out to glass substrate top 2 one by one, the low reflective film 10 was formed, and the low reflective glass plate 30 was produced. In order to investigate the thermal resistance of the low reflective glass plate 30 too, the low reflective glass plate 30 was calcinated for 10 minutes at 630 degrees C with the firing furnace. Each configuration and thickness of the low reflective film are shown in Table 6, and the optical property is shown in Table 7.
[0073]
[Table 6]

A fruit ******** Low refractive index film / quantity refractive-index film/(cutoff film) / light absorption film/(cutoff film) / example of a glass substrate (nm) (nm) (nm) (nm) (nm) (board thickness mm)
— 14 SiO2 /Ta2O5 / SiN/NiSiON/SiN/ MFL 99.9 / 149.2 / 42.8 / 14.9 /28.5 / 4.215 SiO2 /Ta2O5 / SiN/NiSiON/SiN/ MFL 104.9 / 104.7 / 13.3 /11.4/ 54.6 / 4.2

[0074]
[Table 7]

Fruit Permeability A film surface side reflection factor Glass side side ******** Tvis (%) Rfvis(%) 0 degree Rfvis(%) 60 degree The example of Rgvis(%) 0 degree
14 75.4 4.0 9.0 5.315 76.3 4.0 9.0 6.3

[0075] The low reflective glass plate of the examples 14-15 which are the 3rd operation gestalten of this invention so that more clearly than Table 6 Light permeability of all is 75% or more, and the light reflection factor to the vertical-incidence light from a low reflective film surface side is 4% or less further. The light reflection factor to 60-degree incident light from said low reflective film surface side is 9% or less, and the light reflection factor to the vertical-incidence light from said glass plate side is 7% or less.
[0076] As mentioned above, the low reflective glass plate of the 3rd operation gestalt of this invention is a low reflective glass plate with an acid-resisting function also not only to an acid-resisting function but the oblique-incidence light to vertical-incidence light, having the outstanding light permeability. Furthermore, it is the low reflective glass plate which also has thermal resistance. Since the oxygen cutoff film 6 is formed between a glass substrate 2 and the light absorption film 3, the oxygen from the glass substrate 2 at the time of heating can also be intercepted.
[0077] The following things can be grasped from the result shown in the 3rd operation gestalt from the 1st operation gestalt mentioned above.
[0078] First, the light absorption film is described. The acid-resisting function which pressed down 72% or more of light permeability and the effect of rear-face reflection can be collectively realized by using the NiSiON film, the SiC film, the SiCON film, and the light absorption film that consists of a nitride of Ti.
[0079] The acid-resisting function which pressed down the effect of rear-face reflection further can be realized collectively, having the light permeability which was excellent by making n1 and k1 of the light absorption film into the range of 1.6 <=n1 <=3.5 and 0.3 <=k1 <=2.0** furthermore, respectively, and making geometric thickness d1 of the light absorption film into 1<=20nm of 3 nm<=d.
[0080] In addition, about d1, the membranous amount of light absorption cannot become it small that d1 is less than 3nm, and the reflected light reinforcement which comes to a film surface

side from the rear face (opposite side of an antireflection film forming face) of a glass plate cannot make it small. Conversely, light permeability will become low if dl exceeds 20nm.
[0081] Next, the optical multilayers which consist of high refractive-index film of nH=2.0-2.5 and a low refractive index film of nL=1.44-1.48 become possible [reducing the light reflection factor to vertical-incidence light and oblique-incidence light] by setting each geometric thickness dH and dL to dH=60-150nm and dL=85-110nm, and combining it with the above-mentioned light absorption film further.
[0082] Moreover, it can consider as the low reflective glass plate which can bear about 630-degree C heating process by using an SiN film as oxygen cutoff film. Furthermore, in this invention, there is no limit especially of 20 etc.nm or less etc. about the thickness of the oxygen cutoff film which gives thermal resistance so that the 2nd and 3 operation gestalten of this invention may show. Therefore, it is possible by increasing the thickness of the oxygen cutoff film to improve thermal resistance further.
[0083] If it says from the oxygen cutoff engine performance of the oxygen cutoff film, the silicon nitride film is excellent. However, an acid silicon nitride film can also attain the purpose. When an acid silicon nitride film is expressed as SiNxO 1-x, since the oxygen cutoff engine performance becomes large so that it is large, the value of X is desirable. The oxygen cutoff engine performance as oxygen cutoff film is not satisfied as X is less than 0.6. Moreover, in the range of this presentation, it is checking that change of the optical constant of the SiNO film does not influence a reflection property.
[0084] (Example of a comparison) In order to investigate the thermal resistance of the low reflective glass plate to the examples 1-6 mentioned above, it calcinated for 10 minutes at 630 degrees C with the firing furnace, and considered as the examples 1-6 of a comparison. The result is shown in Table 8.
[0085]
[Table 8]

Ratio	Permeability A film surface side	reflection factor Glass side side ********	Tvis (%)	Rfvis(%) 0 degree	Rfvis(%) 60 degree	The example of Rgvis(%) 0 degree
1	80.5	5.5	11.2	8.52	81.9	5.8
2	12.3	8.33	79.9	5.3	10.8	8.14
81.3	5.5	12.9	8.25	82.1	5.9	12.3
8.66	83.0	5.3	12.78.4			

[0086] In these examples of a comparison, since it does not have the oxygen cutoff film, the light absorption film will oxidize and light absorption ability has fallen. Therefore, light permeability is rising about 6%. Furthermore, the light reflection factor to the vertical-incidence light of a filrp surface rose 1.4 to 2.0%, and has exceeded 5% altogether. Moreover, the light reflection factor to 60-degree incident light of a film surface also rose 2.0 to 3.8%, and its thing exceeding 12% has increased. Furthermore, the light reflection factor to the vertical-incidence light by the side of a glass plate also rose 1.5 to 2.3%, and all are it over 8%. Although the above example of a comparison had the outstanding light permeability, the acid-resisting function to vertical-incidence light and oblique-incidence light was not enough.
[0087] By the way, in the above example and example of a comparison, although each film was formed by the sputtering method, you may form with vacuum deposition, without being restricted to this.
[0088] In addition, as optical multilayers prepared on the absorption film in the above example, although it was an example by two-layer [of the high refractive-index film and a low refractive index film], it is also possible to use the optical multilayers of three or more layers instead of this. Generally, by N layer multilayers, since a reflection factor can be set to 0 on the wevelength of N individual, the effectiveness of acid resisting can be heightened by increasing a number of layers.
[0089] However, since a reflection factor begins to increase by whenever [such small incident angle / that it becomes multilayers] as pointed out to the "thin film handbook" mentioned above, it is not necessarily a best policy to use the optical multilayers of three or more layers. Moreover, since a process of form [three or more layer multilayers] increases and it leads also to a cost rise, it is not not much desirable and the configuration by two-layer is more desirable.
[0090] (Application gestalt) The glass laminate as an application gestalt of this invention is

explained below (refer to drawing 4).
[0091] (Application 1) Since it does not have the oxygen cutoff film when using first the low reflective glass plate of the examples 1-6 mentioned above, thermal resistance is missing. Therefore, it cannot heat, after forming the low reflective film.
[0092] Then, the glass plate 2 of two sheets and 2' which cut in desired size and carried out polish processing of the end face first were prepared. This glass plate of two sheets was set to the ring type, and bending was performed with the heating furnace. As a further thermoplastic interlayer 7, the polyvinyl-butyral (PVB) film was put, and it pasted up with the autoclave, and considered as the glass laminate plate 40 (refer to drawing 4).
[0093] Next, on the indoor side face of this glass laminate plate, by the sputtering method mentioned above, the light absorption film 3, the high refractive-index film 4, and the low reflective film 10 that carried out the laminating of the low refractive index film 5 one by one were formed, and the low reflective glass laminate plate 40 for cars was produced.
[0094] (Application 2) Since the oxygen cutoff film is prepared when using the low reflective glass plate of the examples 7-15 mentioned above next, it has thermal resistance. Therefore, it can heat, after forming the low reflective film.
[0095] Then, first, by the sputtering method mentioned above, the laminating of the light absorption film 3, the oxygen cutoff film 6, the high refractive-index film 4, and the low refractive index film 5 was carried out one by one on the glass substrate 2, and the low reflective glass plate 1 was produced. Furthermore, the oxygen cutoff film 6 may be formed between a glass substrate 2 and the light absorption film 3.
[0096] It continued, and cut in the size of a request of this low reflective glass plate, and polish processing of the end face was carried out. Still more nearly another usual glass plate 2' was prepared, it cut in desired size, and polish processing of the end face was carried out. This glass plate 2 of two sheets and 2' were set to the ring type, and bending was performed with the heating furnace. Furthermore, the PVB film was put as an interlayer 7, it pasted up with the autoclave, and the low reflective glass laminate plate 40 for cars was produced.
[0097] The low reflective glass laminate plate 40 for cars produced by applications 1 and 2 was built into the windshield of an actual car, and effectiveness of acid resisting was checked. In addition, any glass laminate plate of the light permeability was 70% or more. Consequently, reflection of not only a perpendicular direction but the direction of slant was fully pressed down, and this glass laminate plate 40 was not the level which becomes offensive to the eye [a reflect lump]. Moreover, light permeability was also what satisfies the specification as a windshield.
[0098] Furthermore, the following invention can also be grasped from the above indication. In the low reflective glass plate which has the low reflective film which carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on one principal plane of a glass plate said light absorption film The low reflective glass plate characterized by being the film which uses the ingredient of the NiSiON (acid nitride of nickel silicide), SiC (silicon carbide), SiCON (acid nitride of silicon carbide), Ta, the nitride [or] of Nb, an acid nitride, or the acid nitrides of Ti or Zr as a principal component.
[0099]
(Effect of the invention) In the low reflective glass plate which has the low reflective film with which this invention carried out the laminating of the light absorption film, the high refractive-index film, and the low refractive index film one by one on one principal plane of a glass plate as explained above Said light absorption film consists of metallic compounds. Said high refractive-index film the refractive index nH and geometric thickness dH Since it is nH=2.0-2.5 and dH=60-150nm and said low refractive index film is the low reflective glass plate which the refractive index nL and geometric thickness dL set to nL=1.44-1.48 and dL=85-110nm The light reflection factor to the vertical-incidence light from said low reflective film surface side 5% or less, The light reflection factor to 60-degree incident light (include angle when making a perpendicular into 0 degree) from said low reflective film surface aide 12% or less, It is the low reflective glass plate which the light reflection factor to the vertical-incidence light from said glass plate side becomes 10% or less, and can reduce the light reflection factor to vertical-incidence light and oblique-incidence light.

[0100] In the low reflective glass plate of claim 2 in the effectiveness of claim 1 Moreover, when [in addition,] it writes N1=n1-i-k [the complex index of refraction of said light absorption film] 1 (n1 expresses the real part of a refractive index with the imaginary part of a refractive index, and k1 expresses an extinction coefficient), since it came out, and it is and n1 and k1 in the wavelength of 550nm made 1.6 <=n1 <=3.5, 0.3 <=k1 <=2.0, and geometric thickness d1 of said light absorption film 1<=20nm of 3 nm<=d, it is the low reflective glass plate which gave the low reflective engine performance, maintaining high light permeability.
[0101] further -- the low reflective glass plate of claim 3 -- setting -- the effectiveness of claims 1 or 2 -- in addition, since said light absorption film was constituted from film which uses the ingredient of the either the nitride of NiSiON (acid nitride of nickel silicide), SiC (silicon carbide), SiCON (acid nitride of silicon carbide), and Ti, Zr, Hf, Ta and Nb or the acid nitrides as a principal component, it is the low reflective glass plate which has good light permeability.
[0102] moreover, the low reflective glass plate of claim 4 -- setting -- the effectiveness of claims 1-3 -- in addition, since light permeability was made into 70% or more, it is the low reflective glass plate with which the glass plate for the windshields of an automobile can be presented, for example.
[0103] further -- the low reflective glass plate of claim 5 -- setting -- the effectiveness of claims 1-3 -- in addition, since the film which has the oxygen cutoff engine performance further was prepared between said light absorption film and said high refractive-index film, it is the low reflective glass plate which could prevent oxidation of said light absorption film and was excellent in thermal resistance.
[0104] moreover, the low reflective glass plate of claim 6 -- setting -- the effectiveness of claim 5 -- in addition, since the film which has the oxygen cutoff engine performance further was prepared between said glass plates and said light absorption film, it is the low reflective glass plate which could prevent oxidation of said light absorption film further, and was excellent in thermal resistance.
[0105] Furthermore, it sets to the low reflective glass plate of claim 7. In the effectiveness of claims 5 and 6, in addition, the film which has said oxygen cutoff engine performance Since it consists of silicon nitride as a principal component, or it consisted of acid silicon nitride expressed as SiNxO 1-x and the value of said X was set to 0.6<=X<1.0 Since penetration of the oxygen from a glass plate to atmospheric air or the light absorption film can be suppressed very low, it is a low reflective glass plate with the thermal resistance which can bear heating processes, such as a bending process and a strengthening process.
[0106] Moreover, in the low reflective glass plate of claim 8, since the ingredient with which said high refractive-index film was chosen from titanium oxide, tantalum oxide, niobium oxide, and tin oxide in addition to the effectiveness of claims 1-3 was used as the film which uses at least one or more sorts as a principal component, it is a low reflective glass plate with chemical durability (chemical resistance) or mechanical endurance (abrasion-proof nature).
[0107] Since it furthermore considered as the film with which said low refractive index film uses oxidation silicon as a principal component in addition to the effectiveness of claims 1-3 in the low reflective glass plate of claim 9, it is the low reflective glass plate excellent in chemical and mechanical endurance.
[0108] moreover -- as the glass laminate plate using the above low reflective glass plate -- claims 1-9 -- with the field of another side of the low reflective glass plate of a publication to either With the low reflective glass laminate plate for cars on which the transparence glass plate other than said glass plate was pasted up by the interlayer made of thermoplastics The light permeability of this glass laminate plate is 70% or more, and since the forming face of the low reflective film was made into the interior-of-a-room side of a car, it is the low reflective glass laminate plate for cars which has the low reflex function which was excellent also to oblique-incidence light, and good light permeability, and was further excellent in endurance.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is a sectional view explaining the 1st operation gestalt of this invention.
[Drawing 2] It is a sectional view explaining the 2nd operation gestalt of this invention.
[Drawing 3] It is a sectional view explaining the 3rd operation gestalt of this invention.
[Drawing 4] It is a sectional view explaining the application implementation gestalt of this invention.
[Description of Notations]
1, 20, 30: Low reflective glass plate,
2 2': Glass substrate,
3: Light absorption film,
4: High refractive-index film,
5: Low refractive index film,
6: Oxygen cutoff film,
7: Interlayer,
10: Low reflective film,
40: The glass laminate plate using a low reflective glass plate,

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[Translation done.]